

# EXTERNAL PEER REVIEW OF THE SCIENTIFIC BASIS OF THE PROPOSED BASIN PLAN AMENDMENT TO ESTABLISH CONTROL OF PYRETHROID PESTICIDES DISCHARGES IN THE SACRAMENTO AND SAN JOAQUIN RIVER BASINS

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Ames, Iowa 50011 – July 6, 2015

## Introduction

I have read the “Proposed Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Pyrethroid Pesticides Discharges – Draft Staff Report”. I have also read the “Methodology for Derivation of Pesticide Water Quality Criteria for the Protection of Aquatic Life in the Sacramento and San Joaquin River Basins, Phase I and Phase II.” I have also read the six “Water Quality Criteria Reports” for permethrin, bifenthrin, cyfluthrin, cypermethrin, esfenvalerate and  $\lambda$ -cyhalothrin. I have also read the guidance for external scientific reviewers provided in Attachment 2 of the letter to Dr. Gerald Bowes from Adam Laputz on May 26, 2015. I have conducted extensive research on synthetic pyrethroids, in insects, aquatic non-target species, including fish, as well as environmental studies on them, beginning in 1976; I have published extensively on synthetic pyrethroids, primarily with my grad students, postdocs and collaborators. My report will address each of the Conclusions 1-5 in the Draft Staff Report, as well as the overall perspective.

## Conclusion 1

The acute and chronic water quality criteria developed by using the UC-Davis methodology are based on sound science; they are logical adaptations from the way the methods were utilized and criteria were developed in 2010-2011. A very broad spectrum of alternative methods were considered and carefully evaluated for their appropriateness, and the selected alternatives are well justified in the draft report. The methods selected and the rationale presented for aqueous concentration and for sediment concentrations are very clear. Specific data on Koc and toxicities for all six of the major pyrethroids being addressed contributes to confidence that fate and availability of residues of each are well understood.

The criteria developed for the pyrethroids will protect the beneficial uses of the waterways; they will also be protective of sensitive species, without being unnecessarily conservative. One important set of information is presented in Table 5-14, which considers the six pyrethroids individually and the possible outcomes for each alternative considered. For consideration of sediment criteria, Tables 5-13 presents valuable information for equilibrium sediment guidelines. The conclusion is sustained as well as possible for sediment, considering the very limited data available for pesticides in sediment. Table 5-16 is an excellent summary of nine factors that must be considered, versus the four most appropriate alternatives for the water quality objectives.

## Conclusion 2

There is every indication that the methodology developed by scientists at UC-Davis is scientifically sound and technically defensible. It presents a very thorough treatment of considering data quantity as well as data quality when developing guidelines for methods; the reports explain the use of toxicity data from short or long time periods, producing protection under both acute and chronic circumstances; determination of criteria that are protective of all species, including sensitive or rare ones, is a crucial tenet in this development of the water quality criteria. Their use of the species sensitivity distribution is quite logical and well documented to be appropriate for risk assessments. While it is preferable to use only data based on measured concentrations, there are distinct benefits to the use of other data (e.g., data from studies with nominal concentrations of the pesticide). The approach the authors present for use of a default acute-to-chronic ratio is valid when there is insufficient toxicity data available; the approach is conservative, but appropriate in those situations.

Physical-chemical data for a compound is extremely important in determining the fate of the chemical and the ecotoxicological effects of compounds (pyrethroids in this case). It is quite encouraging that they specifically address quantitative structure-activity relationships that can be developed for a series of related compounds, such that fate and/or toxicity can be predicted *in silico*, rather than needing to test every new pyrethroid molecule for all its physical-chemical properties and all of its potential ecotoxicology issues. The authors' addressing of mixtures toxicology is important, as multiple stressors occur in almost every real-world body of water. It is a complicated issue, and it is addressed specifically for pyrethroids in the next conclusion, but they lay a very solid foundation for that discussion in the Phase I document. There are also valuable discussions in the methodology documents regarding the possibilities of bioaccumulation and secondary toxicity effects, as well as the goal of protection of endangered and threatened species.

## Conclusion 3

The authors of the draft staff report make a strong case for the additive toxicity approach to evaluation of waters that contain residues of more than one pyrethroid. The concentration-addition model is definitely appropriate for utilization, based on the toxic units approach to the additive effects of multiple pyrethroid insecticides in water samples. While there are some additional effects caused by Type II pyrethroids, the principal mechanism of toxic action at the neuron's sodium channels is the same for both Type I and Type II pyrethroids.

One situation that will not be covered by the additive toxicity model is that of the insecticide synergist piperonyl butoxide co-occurring with a pyrethroid. The synergist is considered to be essentially non-toxic (and it is, compared to any pyrethroid), but it is capable of enhancing the potency of a pyrethroid. It has been used in commercial formulations for over 50 years to increase potency of natural and first-generation synthetic pyrethroids. The question is raised in the Water Quality Criteria Reports. Recently it has been added to formulations of some of the halogenated "photo-stable" pyrethroids, especially permethrin. Not much is known about the persistence of piperonyl butoxide in the environment or about its capacity to enhance toxicity to aquatic non-target organisms, so the document appropriately

does not include it in the additivity formula but mentions it as a possible confounding factor in water or sediment quality. As discussed in the highly informative individual Water Quality Criteria Reports, there is no way to predict or use any data from the presence of synergists or any other non-additive interactions in determining compliance.

#### Conclusion 4

The document addresses the complex question of bioavailability of pyrethroid residues in water and sediment in a relatively straightforward way, especially considering the variables involved in the disposition of pyrethroids in waters and sediments. The ideal situation would be to have measured bioavailability data for each pyrethroid in every type of surface water and every type of sediment, but in fact, little of that information is available. However, there have been major advances in the understanding of pyrethroid bioavailability in recent years. The use of freely dissolved aqueous concentrations of pyrethroids in water is the best way to develop meaningful understanding about bioavailability and uptake of pyrethroids into aquatic non-target species. The use of partition coefficients is a suitable method for estimating bioavailability in aqueous samples, including ones with organic particulates and/or dissolved organic carbon. A realistic bioavailability ratio can be obtained, and it is much more useful than such a ratio derived only from whole-water residues of the pyrethroid(s).

In the realm of sediments, the bioavailability is even more complicated. Considerable information can be generated by batch-equilibrium sorption/desorption studies with natural sediments. Koc values for sediments can provide some indication of the bioavailability of a pesticide, and there are promising techniques utilizing solid-phase micro extraction (SPME) fibers in sediment (and in water) to estimate the availability of pyrethroids to organisms living in sediments. The draft report acknowledges that the bioavailability is often complicated by organisms ingesting food items that contain residues of the pyrethroid. The individual Water Quality Criteria Reports are again very helpful; they address the question of bioavailability for each of the six pyrethroids and discuss some of the data available for specific species in specific experimental situations.

The draft report explains very thoroughly the process of considering all of the possible alternatives for aqueous samples and sediment samples and reaches its conclusions in a logical and quite transparent way. The criteria are likely to be protective of warm and cold beneficial uses of water/sediment systems in California.

#### Conclusion 5

The recommendation of the draft report that total maximum daily loads (TMDLs) should be used for urban waters is well founded. The authors explain the logic by which that conclusion was reached, and what types and amounts of pyrethroids occur in urban wastes. The methods are well understood, and the rationale is explained clearly. The numeric targets for water-column values and for sediment values are likely to be protective of non-target organisms, including sensitive species, and if loading capacities are not exceeded, there should be no serious damage to the beneficial uses of the waters.

## Other Comments

The draft staff report, the documents on the two phases of the methodology, and the six specific documents for individual pyrethroids, all taken together, provide a thorough, carefully developed plan or proposing amendment of the Basin Plan for the Sacramento and San Joaquin Rivers. The plan will be substantially protective of all beneficial uses of the waters, including sensitive species and endangered and threatened species.

It was good that the Implementation section of the draft report addressed vector-control uses of pyrethroids, since there are many of them applied for adult mosquito control. The waste discharges from those operations are already covered under the National Pollutant Discharge Elimination System, so the report makes no further recommendations for those pyrethroids, i.e., under their use for ULV or cold fogging.

A valuable discussion of detection limits is presented in the Surveillance and Monitoring section. The major point is that some sources, e.g., Clean Water Act, list detection limits of pyrethroids from 3 to 5 orders of magnitude higher than some commercial labs or the US EPA Office of Water and Office of Science and Technology. This disparity points to a potential issue in the monitoring of the pyrethroids, depending on which laboratory and what method is used for quantification.

Some specific additions and corrections:

Draft Staff Report:

List of Acronyms and Abbreviations, p. xi – Add POTW

Section 2, p. 25, paragraph 2 – insert “All of the Group III pyrethroids are halogenated, photo-stable chemicals, with the exception of fenpropathrin.”

Section 2, p. 26, line 19 – “Broadcast treatment but not...”

Section 5, p. 51, last lines – One possible mechanism of tolerance or resistance in the *H. azteca* is the selection for an altered sodium channel in the neurons; this is a common mechanism in resistant insects.

Section 5.6.3.1, p. 71 – Sediment Quality Criteria (SQC)

Water Quality Criteria Report for Bifenthrin:

Section 15.2, p. 27, line 25 – “2. This requirement...”

Section 15.2, p. 27, lines 27-28 – “...*Chironomus dilutes* (order: Diptera) is from a different order than *Procladius* sp. (order: Ephemeroptera).”